

SUBTASK 2.3 – CARBON DIOXIDE SEQUESTERING USING MICROALGAL SYSTEMS

Final Report

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	ii
EXECUTIVE SUMMARY	iii
INTRODUCTION	1
OBJECTIVES	2
EXPERIMENTAL	2
Photosynthesis	2
Effects of Flue Gas on Microalgae	3
CO ₂ Uptake and Algal Growth Rates	5
Lighting and Nutrient Requirements	6
Mass Transfer of CO ₂ into Water	7
Design Considerations	9
Flue Gas Delivery System	11
Nutrient Recycle	13
Mixing Systems	13
Other Operational Considerations	15
Algal Harvesting Techniques	16
Beneficial Uses of Harvested Algae	17
Bench-Scale Experiments	18
PRELIMINARY ECONOMIC ASSESSMENT	21
CO ₂ Mass Transfer	21
Algal Growth/Photosynthesis	21
Algal Harvest	22
Economic Analysis Summary	22
CONCLUSIONS	24
REFERENCES	25

LIST OF FIGURES

1	FACT mass transfer prediction	8
2	Schematic of raceway reactor	9
3	Bench-scale process diagram	18
4	Carbon sequestering unit operations	21
5	Beneficial uses of harvested algae	24

LIST OF TABLES

1	Coal Creek Station Flue Gas Data	3
2	Solubilities of Flue Gas Components	7
3	Surface Areas of Calculated Microalgal Cultivation Ponds Using Different Approaches	10
4	Variations in Carbon Dioxide Capture at Different Capture Efficiencies	10
5	Simulated Flue Gas Composition	19
6	Bold's Basal Medium – Major Nutrients	19
7	Preliminary Process Economics Evaluation	23

SUBTASK 2.3 – CARBON DIOXIDE SEQUESTERING USING MICROALGAL SYSTEMS

EXECUTIVE SUMMARY

This project evaluated key design criteria, the technical feasibility, and the preliminary economic viability of a CO₂-sequestering system integrated with a coal-fired power plant based on microalgae biofixation. A review of relevant literature was conducted, and a bench-scale algal-based sequestration system was constructed and operated to verify algal growth capabilities using a simulated flue gas stream.

The bench-scale system was a 20-gallon glass aquarium with a 16-gallon operating volume and was direct-sparged with a simulated flue gas. The flue gas composition was based on flue gas analyses for a 550-MW Coal Creek Power Station boiler in Underwood, North Dakota, which averaged 12.1% CO₂, 5.5% O₂, 423 ppm SO₂, 124 ppm NO_x, and an estimated 50 mg/m³ fly ash loading. The algae were grown in Bold's basal growth medium. Lighting was provided using a two-tube fluorescent "grow-light" bulb fixture mounted directly above the tank. Algal growth appeared to be inhibited in the presence of SO₂ using mixed cultures of green and blue-green cultures of algae. Samples of *Monoraphidium* strain MONOR02 and *Nannochloropsis* NANNO02 algal samples were obtained from the University of Hawaii Culture Collection. These samples did not exhibit inhibited growth in the presence of all the simulated flue gas constituents, but growth rates were somewhat lower than those expected, based on the review of literature.

Samples of harvested algae were analyzed for protein, lipid, and carbohydrate content. A lipid content of 26% appeared to be fairly normal for algae, and it did not appear that large amounts of nitrogen were being fixed and promoting growth, nor were the algae starved for nitrogen. Proteins made up 41% of the total mass, and carbohydrates were assumed to be 33% (by difference).

A preliminary economic analysis showed the costs of an integrated system based on microalgae biofixation to sequester 25% of the CO₂ from a 550-MW coal-fired power plant could be recovered if the value recovered from the harvested algae was approximately \$97. The analysis indicated the potential to produce 2427 tpd of algae at 12% moisture (2136 tpd dry weight). Of this, approximately 876 tpd of protein could be recovered and used as an animal feed. Similarly, an estimated 555 tpd of lipids could be recovered for use in the production of liquid fuels and chemicals. Approximately 705 tpd of carbohydrates would also be recovered. These carbohydrates may be suitable as a fermentation feedstock for the production of alcohols or organic acids.

SUBTASK 2.3 – CARBON DIOXIDE SEQUESTERING USING MICROALGAL SYSTEMS

INTRODUCTION

Global warming due to increased carbon dioxide concentration in the atmosphere is receiving a great deal of attention. Takeuchi (1988) reported that atmospheric increases of carbon dioxide are positively correlated with the amount of fossil fuels being burned. In an effort to retard this increase and, therefore, the greenhouse effect, most industrialized countries have joined in a policy to hold carbon dioxide emissions in the year 2000 to 1990 levels (Hileman, 1992). However, it is not clear if technology exists to achieve this goal.

Selecting the most appropriate technology to limit the amount of carbon dioxide entering the atmosphere has been the major focus of research. One option is carbon dioxide capture and subsequent sequestration into the deep ocean, aquifers or depleted oil and gas wells. However, this is an expensive option (potentially more than doubling the cost of electrical generation via fossil fuels) with no opportunity for profit to displace the cost (Benemann, 1993).

Another option would be to utilize the carbon dioxide. For example, precipitated calcium carbonate (PCC) is gaining acceptance as a replacement for titanium dioxide or kaolin in the manufacture of paper products. PCC is made by controlling the reaction of carbon dioxide with lime.

Carbon dioxide can also be utilized in the following industries: plastics, paint, construction materials, solvents, cleaning compounds, and packaging. However, most of these industries would consume minute quantities of carbon dioxide when compared to the overall amount released annually into the atmosphere (Lipinsky, 1992).

Other methods that limit the amount of carbon dioxide entering the atmosphere include chemical absorption of CO₂ from power plant flue gas, the use of alternative fuels such as natural gas and hydrogen that result in reduced emissions of carbon dioxide, and the use of alternative or renewable energy sources such as wind, solar, nuclear, and geothermal. Limited remaining natural gas reserves do not allow for widespread fuel switching to that resource in the power production industry. Additionally, problems with alternative energy sources include cost, space requirement per unit of energy produced, safety issues, and waste disposal. Problems such as these must be overcome before alternative energy options will be accepted as substitutes for oil and coal.

Biological fixation of carbon dioxide is an attractive option because plants naturally capture and use carbon dioxide as a part of the photosynthetic process. Terrestrial plants sequester vast amounts of carbon dioxide from the atmosphere. However, because of the relatively small percentage of carbon dioxide in the atmosphere (approximately 0.036%), the use of terrestrial plants is not an economically feasible option. On the other hand, discharge gases from heavy industries commonly contain carbon dioxide levels significantly higher than that found in the atmosphere (10%–20%). Therefore, it would be wise to develop strategies to limit this value.

Biofixation of carbon dioxide using microalgae has emerged as a potential option. Microalgae have the advantages of efficient photosynthesis superior to C₄ plants (those plants that form four-carbon stable intermediates in the photosynthetic process; generally associated with agricultural and large terrestrial plants), fast proliferation rates, wide tolerance to extreme environments, and potential for intensive cultures. These advantages promise high performance in the reduction of carbon dioxide (Kurano et al., 1996). Once harvested, microalgae can serve as a product to offset some of the costs that have been incurred. Potential uses for the algae include biodiesel, biofuel for use in electricity production, fodder for livestock, food and chemicals, colorants, perfumes, and vitamins (Michiki, 1995).

OBJECTIVES

The overall objective of this project was to evaluate key design criteria and the technical feasibility of biofixation using microalgae and to develop preliminary economic data. Specific project activities included:

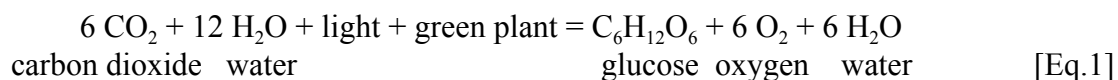
- A review of relevant literature.
- Development of an algal-based sequestration system integrated with a coal-fired power plant.
- Assessment of CO₂ mass transfer.
- Verification of algal growth capabilities using a simulated flue gas stream.
- Determination of algal composition and identification of beneficial uses.
- Assessment of preliminary process economics.

EXPERIMENTAL

Photosynthesis

Photosynthesis is the formation of carbohydrates in the chlorophyll-containing tissues of plants exposed to light. During photosynthesis in green plants, light energy is captured and used to convert water, carbon dioxide, and minerals into oxygen and energy-rich organic compounds.

In many green plants, carbohydrates are the most important direct organic products of photosynthesis. The formation of a simple carbohydrate, glucose, is indicated by the following chemical equation:



Glucose is then converted in the plant to starch and cellulose (which are polymers of glucose), sucrose, amino acids, proteins, fats, pigments, and other organic compounds. Chemical bonds are broken between the carbon and oxygen (in the CO₂) and between the hydrogen and oxygen (in the water), and new chemical bonds are formed in the organic compounds. More energy is required to break the bonds of CO₂ and H₂O than is released when the organic compounds are formed. This excess bond energy accounts for the light energy stored as chemical energy in the organic compounds formed during photosynthesis. The amount of light, the carbon dioxide concentration, and the temperature are the three most important environmental factors that directly affect the rate of photosynthesis. Plant species and plant physiological state also affect the rate of photosynthesis.

The energy efficiency of photosynthesis is defined as the ratio of energy stored as organic compounds to the energy of light absorbed. The maximum efficiency of glucose production is about 31%. Energy stored in the chemical bonds of the organic compounds will be released when the organic compound is combined with oxygen during combustion or when metabolized by an animal or other organism.

Effects of Flue Gas on Microalgae

To understand the environment the algae might be exposed to, data were obtained from the Coal Creek Station power plant located in Underwood, North Dakota, for the period of August 4–7, 1998. The flue gas components of particular concern are carbon dioxide (CO₂), sulfur dioxide (SO₂), nitrogen oxides (NO_x) oxygen (O₂), other trace gases, metals, and ash at elevated temperatures. Table 1 lists some average characteristics of the flue gas during the sampling interval.

Table 1. Coal Creek Station Flue Gas Data

	Stack Temp., °F	Stack CO ₂ , %	Stack O ₂ , %	Stack SO ₂ , ppm	Stack NO _x , ppm	Flue Gas Flow Rate, KSCFM
Average	239.5 (115.3°C)	12.1	5.5	422.9	123.6	1712.6
High	251.9 (122.2°C)	12.4	6.6	450.5	142.4	1768.3
Low	228.4 (109.1°C)	11.8	4.7	399.3	106.2	1487

Much work has been done on the effect of different flue gas constituents on microalgal growth rates and carbon dioxide fixation. Typical power plant flue gases have carbon dioxide levels ranging from 10%–15%. At the typical carbon dioxide percentages, microalgae show no signs of significant growth inhibition. Furthermore, studies have shown that microalgae respond better to increased carbon dioxide concentrations, outgrowing (on a biomass basis) microalgae exposed to only ambient air (Maeda et al., 1995; Brown, 1996).

Sulfur oxides, particularly SO₂, can have a significant effect on the growth rates and health of the microalgae. Of greatest concern is the effect SO₂ has on the pH of the microalgal growth medium. When the SO₂ concentration reaches 400 ppm, the pH of the medium can become lower

than 4 in less than a day, which significantly affects the productivity of the microalgae. However, if the pH is maintained at 8 using NaOH, the productivity does not decrease (Matsumoto et al., 1997). Other researchers have demonstrated tolerances to sulfur oxides at approximately half of what Matsumoto and coworkers (1997) demonstrated (Brown, 1996; Zeiler et al., 1995). *Nannochloris* sp. (NANNO02) was found to be resistant to 50 ppm SO₂, but without pH control, 300 ppm SO₂ inhibited growth within 20 hours (Negoro et al., 1991).

Nitrogen oxides also comprise a significant portion of power plant flue gas. As with the sulfur oxides, nitrogen oxides can affect the pH of the algal medium, but to a lesser degree. Microalgae have been shown to tolerate and grow in a medium containing 240 ppm NO_x, with pH adjustment. Brown (1996) and Zeiler and coworkers (1995) also demonstrated that microalgae are not growth-inhibited by the presence of 150 ppm NO. Negoro and coworkers. (1991) found that NANNO02 grew in the presence of 300 ppm NO after a considerable lag time. A point of interest is that the nitrogen oxides can serve as a nitrogen source for the microalgae. NO is absorbed into the medium and oxidized into NO₂ in the presence of oxygen (Negoro et al., 1991). The greater the oxygen content of the medium, the greater the NO₂ production and microalgal productivity rates (Matsumoto et al., 1997; Brown, 1996). However, the presence of elevated concentrations of oxygen results in algal photorespiration, which inhibits microalgal growth.

The effect of soot dust and ash containing heavy metals has received limited attention. Matsumoto and coworkers (1997) confirmed that when soot dust concentration is greater than 200,000 mg/m³ (0.2 g/L), algal productivity is influenced. It is rare for the soot dust concentration to reach such an elevated value since it is most commonly on the order of 50 mg/m³ (5×10^{-5} g/L). The same argument can be applied to the presence of trace heavy metals. Higher concentrations can affect algal productivity, but only in rare situations will the concentrations exceed those that will result in a significant impact.

When the flue gas is taken as a whole and applied to the microalgae, i.e., not in individual components, the results do not change much. Some microalgal strains have shown tolerance to a medium containing a carbon dioxide concentration of 13.6%, 200 ppm sulfur dioxide, and 150 ppm NO (Brown, 1996; Zeiler et al., 1995). Matsumoto and coworkers (1995) identified one marine species (*Tetraselmis* sp.) that was cultivated without difficulty while subjected to flue gas containing 14.1% CO₂, 1.3% O₂, 185 ppm SO_x, and 125 ppm NO_x. Other strains of microalgae have shown similar tolerances to carbon dioxide and NO_x, but less tolerance to the sulfur oxides (Maeda et al., 1995; Yanagi et al., 1995).

Another concern with the flue gas is the elevated temperatures. In a commercial application, flue gas from the desulfurization scrubbers would be sent to the CO₂ sequestration ponds for treatment. Temperatures exiting the scrubbers at the Coal Creek Station are approximately 140°F (60°C) (data not shown). Therefore, microalgae would need to exhibit tolerances at temperatures of this magnitude. Although most organisms cannot survive at these higher temperatures, some cyanophycean algae have been shown to grow at 176°F (80°C).

Overall, the microalgae have shown great tolerances to harsh environments. Experimental conditions from other studies compare favorably to the stack operating conditions at the Coal Creek Station. The most important concern appears to be the high level of SO_x in the stack gas in combination with the elevated temperatures. Bench-scale tests would need to be performed to confirm the effect of the stack gas on the productivity of various microalgae.

CO₂ Uptake and Algal Growth Rates

To determine the viability of using microalgae as a carbon dioxide sequestration option, carbon dioxide fixation and microalgae growth rates have been studied. It should be noted that current data were taken from microalgae grown in specially constructed photobioreactors (PBRs), or growth chambers, except where it is otherwise specified.

Microalgal growth rates ranged from approximately 15–25 g dry biomass per m² (basal area) per day (g dry wt m⁻² day⁻¹), with reports of short-term rates of 50 g dry wt m⁻² day⁻¹ (Chelf et al., 1993). In terms of growth per reactor volume, the growth rates ranged from 0.1–1.2 g dry wt L⁻¹ day⁻¹, with maximum cell concentrations ranging from 0.7–14.4 g dry wt L⁻¹ (Kurano et al., 1996; Michiki, 1995). Microalgal doubling time (defined as the amount of time for the biomass to double in weight) has been shown to be on the order of hours (2.4–24) for most microalgal samples studied (Sakai et al., 1995; Kurano et al., 1995; Michiki, 1995).

Matsumoto and coworkers (1997) demonstrated that microalgal productivities on a large scale were comparable to productivities achieved during small-scale testing (approximately 8–10 g dry wt m⁻² day⁻¹).

In order to obtain high algal production rates, many of the referenced studies harvested the biomass daily. If unharvested, production rates will reach a peak and then decline with increasing biomass concentration because of reduced available light (mutual shading) and depletion of nutrients (Nishikawa et al., 1992). Therefore, harvesting is an essential part of maintaining high microalgal productivity rates.

Benemann (1997) asserts that the microalgae growth rates that occur in bioreactors and small-scale ponds cannot be expected in full-scale operating sequestration ponds. Photosynthetic visible light conversion efficiencies in laboratory experiments are often 20%–24%, whereas maximum conversion efficiencies of higher plants (such as sugar cane) grown at optimum conditions are only 7%–8%. The conversion efficiencies of microalgae are not expected to exceed those of the higher plants. And to achieve those efficiencies would require development of techniques to maintain the original algal strains and ward off invasion by other algae, zooplankton, and infections.

Data for carbon dioxide uptake were more limited than the growth data. Watanabe and Hall (1995) reported a carbon fixation rate of 14.6 g C m⁻² (basal area) day⁻¹ at a growth rate of 30.2 g dry wt m⁻² day⁻¹. Kurano and coworkers reported a range of 0.65–4.0 g CO₂ L⁻¹ day⁻¹ at growth rates of 0.4–2.5 g dry wt L⁻¹ day⁻¹. Results were corroborated using direct measurements of the inlet and outlet gas streams and indirectly estimated from the carbon content of the cell and the cell growth rate.

Weissman and Tillett (1992) demonstrated the capture of carbon dioxide by large pond-type systems. When operating under optimum conditions, the capture efficiency has been shown to be as high as 99% (Weissman and Tillett, 1992; Zeiler et al., 1995).

These results show the potential for using microalgae for carbon dioxide fixation. The microalgae have high growth (production) rates and accumulate CO₂ approximately half as fast (and faster) as it is growing.

Lighting and Nutrient Requirements

The basic nutrient requirements of the microalgae include carbon dioxide, nitrogen and phosphorus along with trace nutrients (minerals and metals). Flue gas supplies the carbon dioxide and has the ability to supply some of the nitrogen, as previously discussed. However, it has been demonstrated that the nitrogen contribution from the flue gas is insufficient to maintain stable growth rates (Weissman and Tillett, 1992). Therefore, nitrogen, phosphorus, and trace nutrients can be added and maintained as necessary with proper engineering.

The most appropriate light source and method of introduction to the biomass has been the focus of much research. In the case of the PBRs, the design of the PBR is the most important consideration for light penetration and distribution. Tubular PBRs achieve a higher photosynthetic efficiency (PE; defined as how efficiently radiant energy is converted into chemical energy within the microalgae) than flat PBRs (Tredici and Zittelli, 1998). The curved surfaces more evenly distribute the light within the reactor by maximizing the illumination surface-to-volume ratio (Ogbonna and Tanaka, 1997; Watanabe and Hall, 1996). Other designs include spiral and helical PBRs (Watanabe and Hall, 1995; Watanabe and Hall, 1996).

Outdoor cultivation ponds offer another option for mass production of microalgae. An outdoor cultivation pond, although often simpler in design, offers some drawbacks that must be taken into consideration when dealing with light intensity and distribution within the pond.

Studies have shown that it can be difficult to obtain high productivity in open ponds because the temperature and light intensity vary throughout the day and year (Ogbonna and Tanaka, 1997; Acien Fernandez et al., 1997). In addition, even during bright summer days, outdoor algal cultures have been shown to be light-limited (Tredici and Zittelli, 1998). Therefore, it is suggested that to achieve maximum productivity, it is desirable to have artificial sources of light for nights and cloudy days (Ogbonna and Tanaka, 1997). However, the intensity of the light cannot simply be increased. Increased light intensities result in poor P.E. values due to the light saturation effect. The light saturation effect accounts for the fact that a twentyfold increase in the incident energy results in only a fourfold increase in the amount utilized by the algae (Tredici and Zittelli, 1998).

If sunlight is the sole source of radiant energy, poor light penetration into the pond becomes a problem. One solution is biomass stirring, used to expose bottom algal cells to sunlight. The beneficial effects of stirring are without question (Tredici and Zittelli, 1998), but one must take care to minimize hydrodynamic/shear stress on the microalgae, which can significantly decrease productivity (Ogbonna and Tanaka, 1997; Palsson, 1995). Other solutions might include the use of

“spatial dilution of light” (Tredici and Zittelli, 1998), i.e., distribution of the impinging photon flux on a greater photosynthetic surface area, generally used to distribute sunlight deeper into the culture through the use of specifically placed lenses, glass or plastic cones, optical fibers, and quartz or acrylic rods. Alternative light sources, such as the use of artificial light and lights of different color (frequency), and different light configurations can also be utilized (Ogbonna and Tanaka, 1997; Palsson, 1995).

Mass Transfer of CO₂ into Water

The amount of flue gas a cultivation pond accumulates depends upon the solubility of the flue gas components in water. The target flue gas is carbon dioxide, but the others (sulfur oxides, nitrogen oxides, oxygen, etc.) must be simultaneously considered. Table 2 lists the solubilities of some major flue gas constituents in water (Dean, 1992).

Table 2. Solubilities of Flue Gas Components

Component Gas	Temperature, °C	Solubility, cc/mL H ₂ O
Carbon Dioxide (CO ₂) ¹	0	1.713
	20	0.878
	60	0.359
Sulfur Dioxide (SO ₂) ²	0	79.789
	20	39.374
	40	18.766
Nitric Oxide (NO) ¹	0	0.07381
	20	0.04706
	60	0.02954

¹ Measured at standard conditions (0°C and 760 mmHg) – pressure of the gas without the water vapor is 760 mm Hg.

² Measured at standard conditions (0°C and 760 mmHg) – pressure of gas plus water vapor is 760 mm Hg.

It is worth noting that the reported values represent solubility of that single component in water without the presence of the others. Data for the solubility of individual components of a flue gas, in the presence of the entire flue gas, is not available. Moreover, as the dissolved gases react with water and oxygen, new species are formed that have their own solubility and potential impact on the algal growth system. Therefore, bench-scale testing is necessary to determine solubilities of the combined flue gas constituents.

Another point of interest is that increased temperatures decreased the solubility of the gases in water. Therefore, it would be advantageous to substantially lower the temperature of the flue gas to approximately ambient conditions before introduction into a cultivation pond.

The Energy & Environmental Research Center (EERC) investigated the combined solubility of major flue gas constituents using the Facility for the Analysis of Chemical Thermodynamics (FACT) computer software program. The program is an integrated thermodynamic database coupled

to programs developed to calculate multicomponent multiphase equilibria based on a minimization of Gibbs' free energy. Once the initial system composition and pressure is specified, FACT determines equilibrium concentrations of solid, liquid, and gas species over a selected range. The program estimates the concentration and state (solid, liquid, or gas) of all species present based on bulk coal ash chemistry in contact with a typical combustion gas environment. The FACT program is able to provide estimates of the amount, composition, and viscosity of liquid phases present as a function of temperature.

Input included the major gas-phase constituents (CO_2 , O_2 , SO_2 , NO_x , and N_2) from flue gas in contact with an aqueous solution containing nutrients in Bold's basal growth medium. Volume:volume ratios of gas:liquid ranging from 1 to 12 were modeled. The model predicted that a 3:1 gas:liquid ratio is required to result in 100% mass transfer of CO_2 from the gas to liquid phase. The model also predicted that under those conditions, all of the O_2 , SO_2 , NO_x , and even mercury would be in solution. The FACT model predicted that at gas:liquid ratios of 6:1, about half of the flue gas CO_2 goes into solution (50% mass transfer), and at a gas:liquid ratio of 12:1, only 10% of the flue gas CO_2 is solubilized. Model output for CO_2 solubilization is illustrated in Figure 1. The values obtained from the model were used to calculate a scrubber liquid flow rate needed to remove CO_2 to a specific level. In all cases modeled, SO_2 , NO , and Hg were 100% in the liquid phase.

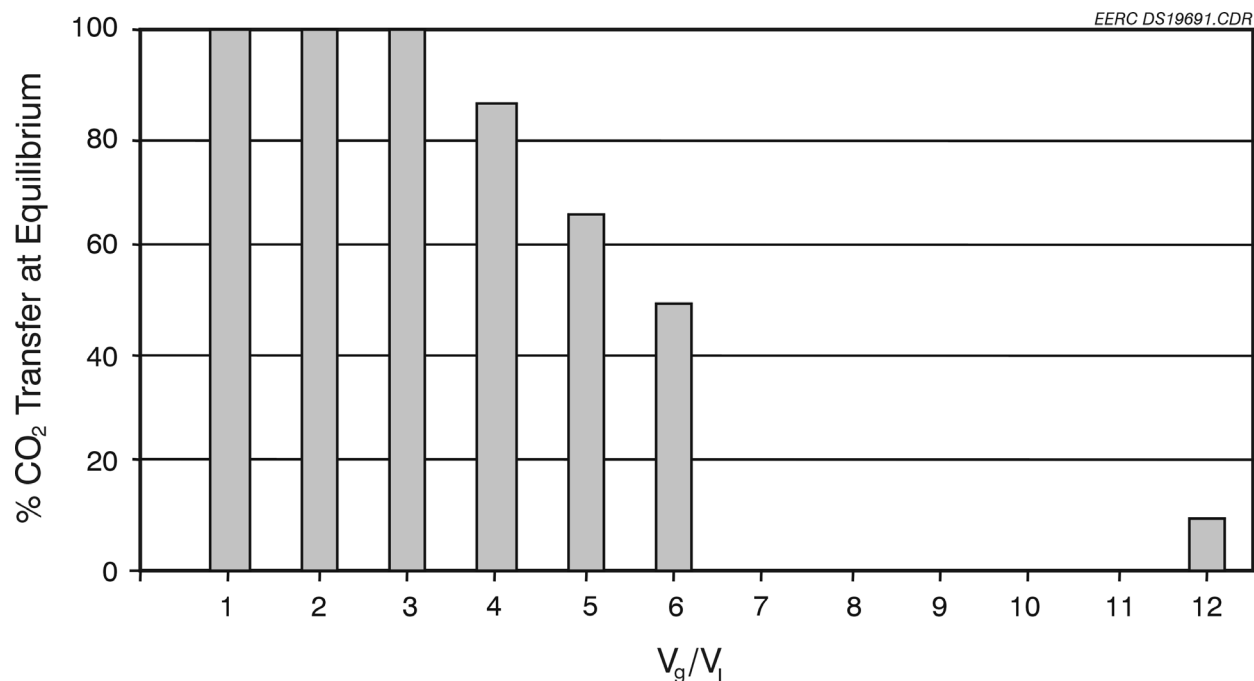


Figure 1. FACT mass transfer prediction.

However, Hg is soluble in the oxidized form, and it has been observed that anywhere from 10% to 90% is oxidized. Since the oxidation of Hg is a rate-limited step, it may be less than 100%. The total Hg possible is 410 gms/day for the full flue gas stream. CO₂ was 100% in the liquid phase from Vg/Vl = 1–3. The percent CO₂ in the liquid phase begins to fall after a Vg/Vl of 3. The goal of removing 25% of the CO₂ can be accomplished by scrubbing one-half (856,000 scfm) the flue gas flow rate for 12 hr of sunlight (one-half day) with 2,135,000 gpm of liquid, or 2493 gal/1000 scfm.

Design Considerations

The preliminary design discussion that follows is based on a design known as a raceway reactor (see Figure 2).

Based on the Coal Creek Station values for gas flow rate and stack carbon dioxide percentages (1712.6 KSCFM and 12.1% CO₂) and 50% bypass of the microalgal cultivation pond (i.e., 50% of the flue gas is sent directly to the stack), a preliminary sizing estimate was performed on a microalgal cultivation pond. Three different approaches were taken and the results compared. Approach No. 1 used microalgal carbon dioxide uptake rates based on laboratory measurements using PBRs. Approach No. 2 used an estimate that microalgae require only 140–200 pounds of water per pound of carbon fixed, even in open ponds (based on average pond evaporation rates) (Brown and Zeiler, 1993). Approach No. 3 used the solubility of carbon dioxide in water.

Pond depth will be a critical factor in the design of both commercial and bench-scale operations. The ponds are generally built shallow, with depths not exceeding 90 cm (2.95 ft). At greater depths, mutual shading and microalgal settling become important and will result in decreased growth and fixation productivities. According to Kadam (1997), pond sizes should not exceed 20 ha each (a larger pond would be difficult to operate). Kadam estimated a pond surface area

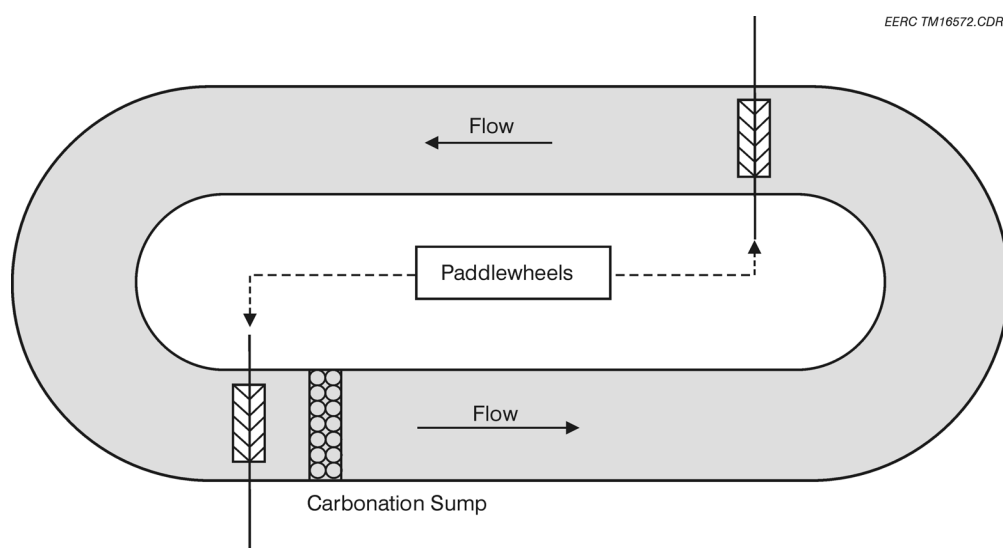


Figure 2. Schematic of raceway reactor.

of 14,000 ha for a 500-MW power plant. Table 3 gives pond surface areas for depths not exceeding 90 cm.

Table 3. Surface Areas of Calculated Microalgal Cultivation Ponds Using Different Approaches

Depth, m (ft)	Approach No. 1 Area, ha (acre)	Approach No. 2 Area, ha (acre)	Approach No. 3 Area, ha (acre)
0.1 (0.33)	3880 (9582)	360 (889)	11,774 (29,081)
0.3 (0.98)	1293 (3194)	120 (296)	3925 (9694)
0.5 (1.64)	776 (1916)	72 (178)	2355 (5816)
0.7 (2.30)	554 (1369)	51 (127)	1682 (4154)
0.9 (2.95)	431 (1065)	40 (99)	1308 (3231)

The following assumptions were made for the each of the approaches in the calculation of pond surface areas:

Approach No. 1: 50% bypass; carbon dioxide uptake of 2.0 g CO₂/L-day (one day)

Approach No. 2: 50% bypass; 170 lb H₂O per lb carbon fixed (based on evaporation)

Approach No. 3: 50% bypass; CO₂ solubility of 36 cc CO₂/100 mL H₂O at 60°C (one day)

The pond surface areas in Table 3 assume that 100% of the carbon dioxide entering the pond system will be captured by the microalgae. Assuming 50% bypass, as in Table 3, this corresponds to 149.2 million ft³ CO₂ (approximately 8550 tons CO₂) captured per day. However, because of the high flow volumes and/or low carbon dioxide solubility, it is unlikely that 100% of the carbon dioxide can be captured. Table 4 lists carbon dioxide volume and mass capture rates corresponding to varying CO₂ capture efficiencies.

Table 4. Variations in Carbon Dioxide Capture at Different Capture Efficiencies

Carbon Dioxide Capture, %	Volume of Carbon Dioxide Captured, million ft ³ CO ₂ /day	Mass of Carbon Dioxide Captured, tons CO ₂ /day
100	149.2	8549
90	134.3	7694
75	111.9	6412
60	89.5	5129
45	67.1	3847
30	44.8	2565
15	22.4	1282

Calculations were also performed for the upper and lower limits of bypass percentage, carbon dioxide uptake, water required per pound of carbon fixed, solubilities at different temperatures, and greater depths. These values are tabulated in Appendix A along with sample pond area requirement calculations. The above assumptions are based on the averages of the limits, except for the solubility value shown for Approach No. 3. The solubility value was chosen because of the effect of the hot flue gas on the temperature of the water in the sequestration pond.

Flue Gas Delivery System

Weissman and Goebel (1987) investigated different alternatives for introducing and storing carbon dioxide in a microalgal growth medium. The capacity for carbon dioxide storage in a growth medium is important because it determines the number of carbonation stations required for a pond of specified size, depth, and liquid velocity or, alternatively, the maximum pond size serviceable with one CO₂ station. The first observation is that water chemistry will have a significant impact on the amount of carbon dioxide stored. Carbon dioxide storage capacity of the medium depends on the alkalinity and pH range of operation. The absorption of CO₂ into alkaline waters may be accelerated by one of two major uncatalyzed reaction paths: the hydration of CO₂ and subsequent acid:base reaction to form bicarbonate ion, and the direct reaction of CO₂ with the hydroxyl ion to form bicarbonate. The rate of the former reaction is faster at pH values below 8, while the latter dominates above pH 10. Between pH 8 and 10, both can be important. However, it has been shown that regardless of the reaction path, there is no appreciable chemical enhancement unless the reactions are catalyzed.

An alternative way of controlling CO₂ input is to control the flue gas flow rate so a specified amount of carbon is stored. This could be accomplished with a computerized control loop that adjusts input loading based on changes in carbon storage as a function of pH change. One would want to use such a system in situations where alkalinity is low, requiring many carbonation stations per unit area.

Weissman and Goebel (1987), using both pure CO₂ and 15% CO₂ (as in a flue gas), studied two different types of carbonation systems. The practical efficiencies are assumed to approach 95% for stripping pure CO₂ input gas and 80% for flue gas. The first carbonation system studied was a covered area carbonator, or bubble cover. By covering a small percentage of the pond area with a membrane-covered structure submerged at its edges, gas transfer can occur passively through the pond surface under the cover. The cover serves to trap a gas volume with a high concentration of CO₂. The percent pond coverage depends on the transfer rate of CO₂ under the cover. To increase transfer efficiency, the roughness coefficient under the cover can be increased by increasing the roughness of the underside of the cover and placing it in partial contact with the water. This “rippled” cover design can be developed by using corrugated material for the cover.

Results of the bubble cover analysis showed that treating a gas containing low concentrations of CO₂ (i.e., flue gas) would require a high coverage percent in all cases. Therefore, the bubble cover concept is feasible only when pure CO₂ is used. It was assumed that a covered-area carbonator is practical only if the percent coverage is low (about 2%). This may be achievable with a smooth cover

in shallow, fast-mixed ponds, in 20-cm (7.87 in.)-deep ponds if the area under the cover is made shallow, or in moderately deep, moderately mixed ponds if a rippled cover is used.

An alternative way of transferring CO₂ into pond water is to inject the gas at or near the bottom of a sump that spans all or part of the channel. Capital and operating costs are sensitive to sump depth, which determines both transfer efficiencies and pressure drops. The carbonation sump may be feasible for both pure CO₂ and flue gases because gas transfer is quantitatively different in sumps. For bubble covers, the flow hydraulics under the cover determine the mixing that is needed to disrupt the thin film which effects transfer and mixes the dissolved gas with the bulk liquid. In sumps, movement of the bubble swarm relative to the flowing liquid “renews” the transfer surface. Thus behavior of the bubble swarms determines transfer rates.

It has been demonstrated that size distribution of the bubbles leaving the sparger may initially be a strong function of the sparging method. However, as bubbles of differing size rise through the fluid at differing velocities, coalescence of the smaller bubbles occurs. On the other hand, fluid forces will break up bubbles above a certain critical diameter (about 0.5 cm in water). Therefore, the coalescence and redispersion of bubbles in the rising swarm leads to a steady-state size distribution a short distance above the sparger. This equilibrium size will depend on such factors as sparger orifice, gas flow rate, and bubble coalescence factors (salinity, surfactants, and turbulence).

Once the unit bubble size is determined, fractional absorption per unit time (k_g) from the gas phase can be determined. Although no literature was found that was directly applicable to CO₂ transfer, a well-established mass transfer correlation can be used to calculate the k_g for CO₂ transfer from that of O₂. The k_g calculated for carbon dioxide was approximately 0.125 sec⁻¹. In other words, for this value of k_g , a swarm of gas bubbles rising through unsaturated liquid would lose about 12.5% of their remaining carbon dioxide each second. Knowing k_g , the time required for 80% or 95% carbon dioxide transfer can be calculated. And by knowing the rise velocity of the swarm, a sump depth can be determined for the required carbon dioxide transfer.

The use of unpurified power plant flue gas would most likely require deeper sumps. For example, introduction of pure carbon dioxide at a liquid flow velocity of 20 cm/sec will require a sump depth of 1.5 m and result in a carbon dioxide transfer efficiency of 95%. By way of comparison, using a simulated flue gas (15% CO₂) at a liquid flow rate of 30 cm/sec will require a sump depth of 13.4 m and result in a carbon dioxide transfer efficiency of only 90%. In addition, flue gas recycle ratios to achieve an overall removal of 80% are consistently and significantly higher than the recycle ratios necessary to achieve 90% and 95% overall removal using pure CO₂ under concurrent, lateral, and countercurrent flows. And unless the power plant is actually within about 1 km of the pond system, the transport of dilute CO₂ becomes too expensive because the piping and blower system for delivering the carbon dioxide to the ponds is a major capital and operating cost for the overall system (Benemann, 1993). According to Kadam (1997), it is economically feasible to deliver purified CO₂ to ponds that are up to 100 km from the power plant.

If carbon dioxide purification is deemed necessary, conventional processes are available. Kadam (1997) recommends monoethanolamine extraction, compression, and dehydration of CO₂ prior to transport. However, an improved CO₂ recovery process has been demonstrated by Mitsubishi

Heavy Industries of Japan (Rawn-Schatzinger, 1999). The two-stage boiler flue gas recovery process improves on conventional CO₂ recovery operations by utilizing new amine-based solvents to reduce the regeneration energy requirements by approximately 20% and through the development of a new absorber packing to reduce internal pressure losses, resulting in significant power savings with respect to the flue gas blower. Results of this process show greater than 90% CO₂ recovery, with a CO₂ purity of 99.9%. The process has been shown to be energy efficient, with a 25% cost reduction in energy production and a one-seventh reduction in operating pressure.

Nutrient Recycle

An opportunity exists for significant recycling of nutrients, especially with respect to carbon, through anaerobic digestion. Weissman and Tillett (1987) studied large outdoor cultivations of microalgae for the purpose of producing fuels. It was reported that 60% of the algal biomass existed as lipid. The lipid fraction can be increased by limiting the nitrogen supply to the microalgae (Negoro et al., 1991). Of the lipid portion, 90% would be extracted for fuel production, which would result in a residue that contained 46% of the algal carbon; 65% of this residue would degrade in the lagoon to methane and carbon dioxide in a ratio of 6:4. The other 35% would split between the two liquid components of the lagoon: the sludge and the lagoon water. Both the gas components and the lagoon water (effluent) can be recovered.

The gas collected from the anaerobic digester could be combusted to produce electrical power. The resultant flue gas is about 14% carbon dioxide and contains 31% of the original algal carbon. The flue gas could then be combined with the pure carbon dioxide input in a ratio of 7:1, which yields a gas containing 35% carbon dioxide. If this is then injected into the ponds with 90%–95% efficiency, and the dissolved carbon in the digester effluent is recycled back to the ponds, the result is a decrease in overall carbon dioxide input from 2.4 kg/kg algae to 1.6 kg/kg algae which could result in significant cost savings (Weissman and Tillett, 1987).

It has also been reported that in addition to the 33% carbon recycle, other core nutrients such as nitrogen and phosphorus can be recycled at 75% and 50%, respectively (Weissman and Tillett, 1987). Another advantage of the anaerobic lagoon is the significant reduction in quantity of solids to be dried and disposed of.

Mixing Systems

Some form of mixing is required to maintain cells in suspension, to prevent thermal stratification, and to disperse nutrients. Three options were analyzed for mixing the ponds: paddlewheels, airlift, and combined carbonation and mixing in sumps.

The paddlewheel has emerged as a preferred method for mixing high-rate ponds for the following reasons:

- 1) They are well matched to the pumping requirements of high-rate ponds in that they are high-volume, low-head devices.

- 2) Their gentle mixing action minimizes damage to colonial or flocculated algae, which improves harvestability.
- 3) They are mechanically simple, requiring a minimum of maintenance.
- 4) Their drive train can easily be designed to accommodate a wide range of speeds without drastic changes in efficiency.
- 5) They do not require an intake sump, but simply a shallow depression for maximum efficiency.

The following are disadvantages associated with paddlewheels:

- 1) The paddlewheel itself must be custom designed.
- 2) They are large relative to other types of mixers, especially at higher heads.
- 3) They are fairly expensive, although not particularly so for a low-shear pump type.
- 4) For practical purposes, the maximum head is limited to 0.5 meters. This would be a constraint only in very large (>20 hectares) ponds or at high velocities (>30 cm/sec) in moderate-sized ponds.

Gas lift mixing is an alternative that does not require large, custom-fabricated mechanical parts. The lift is determined by the ratio of gas and liquid flow rates through the sump and by the ratio of the velocities. Decreasing the ratio of gas velocity to liquid velocity increases both the efficiency and the lift.

The airlift discussion is limited because an interesting option exists in systems for which carbon dioxide is supplied via in-pond sump. Potential exists for combining the carbonation and mixing systems. When flue gas is used for carbonation, the lift may be supplied by the carbonation alone for part of the time, but most likely an air supply system would need to be available to substitute for the flue gas when carbon demand is low and during the nighttime. When pure CO₂ is used, supplementary air would always be required.

The combination of gas lift mixing and carbonation requires matching of the mixing system performance to constraints set by the carbonation. Airlift efficiency increases with increases in liquid velocity. However, the injection efficiency of CO₂ increases only with gas bubble rise time, which decreases as liquid velocity increases unless the height of rise is made greater. With pure CO₂, the lift attainable was much lower than required to mix the pond, while with the flue gas, the lift was much greater than necessary. When carbon dioxide is recycled from the digester flue gases and mixed with pure CO₂, a good match is achieved between transfer and mixing needs during times of maximum carbon demand.

When purified CO₂ is used as the mixing gas, the total gas flow rate is restricted to that required to carbonate the pond. It was concluded that the gas flow rate would be low enough to attain a transfer rate of 25% sec⁻¹ and a gas-to-liquid flow rate ratio of about 0.02 for sumps without recycle and 0.056 for shallower sumps with recycle. The former sumps were 4.2 m deep, and the latter were only 1.5 m deep. The lift provided by these configurations was only 4 cm (one-fifth of that required). Only by increasing the pond size dramatically can the lift attainable be increased faster than the lift required. Increasing the liquid velocity, accomplished by baffle adjustment can also increase the lift. For smaller pond sizes, the mismatch between lift needed and pure CO₂ required for carbonation is too great. If long draft tubes are used, the rise time of the bubbles still needs to be 12 seconds for 95% stripping efficiency. The tubes would need to be 20 m deep (long) and have an area of one-tenth the channel cross section to provide a lift of 20 cm (Weissman and Goebel, 1987).

With flue gas, as with dilution of the CO₂ by air, the lift increases with the increased flow. It can be assumed that the increase in gas flow rate would lead to an increase in average bubble size and, hence, an increase in sump depth needed to strip CO₂ effectively. For flue gas, at a maximum average carbon demand of 8 g/m²/hr, the lift attainable in a 6.2-m-deep sump (80% injection efficiency) is over 74 cm. The lift can be lowered by carbonating 18–24 hours per day into a medium containing sufficient alkalinity to minimize pH fluctuations in the upward direction during the day and downward during the night. This lowers the lift to 39 cm. In order to reduce lift enough, baffling would need to be arranged to lower liquid velocity in the sump.

The most promising possibility for combining processes would be to supply carbon dioxide as flue gas over 24 hours during the high-productivity months but only over 12 hours when productivity is lower. During these times, air would substitute for the flue gas at night, when mixing speeds could be lower, reducing power input.

Given the uncertainties in the parameters for both carbonation and gas lift taken alone, design and cost estimation of a combined system must await results of pilot-scale experiments. In all cases, any system combining air lift and carbonation must use CO₂ with the highest efficiency, essentially as high as carbonation alone would achieve. For experimental purposes, both paddlewheel and airlift mixing systems were designed. The airlift system is comprised of three draft tubes, each 2 m long. The calculated efficiency for this configuration was the same as for the paddlewheel system, about 40%. No specific design was specified for a combined gas lift mixing-carbonation system. The gas transfer parameters were not known well enough to formulate a meaningful design at the time this report was written.

Other Operational Considerations

One proposed method to increase microalgal growth and, therefore, carbon dioxide fixation productivities is addition of methanol to the growth medium. When a dilute mixture of methanol was introduced to microalgae, growth doubled (Dale, 1994; Nonomura and Benson, 1992).

The plant response to methanol has been identified. The first effect is a substantial reduction of evaporation of water. This means there is more water in the plant and a higher internal pressure, known as turgidity. The increased turgidity causes an increase in the opening of the stomata (pores

of the plant) which permits increased absorption of carbon dioxide. This increased supply of carbon dioxide to the plant permits increased rates of plant growth. However, overuse of methanol can be toxic to the plant so work needs to be performed on application rates and methods. In addition, methanol is toxic to shaded plants, and more research is needed to determine how to use methanol in cold climates (Dale, 1994). With respect to the microalgal fixation project, the interaction of methanol with the flue gas and its effect on the microalgal productivities would need to be studied.

Another consideration is to optimize the microalgal carbon dioxide uptake through acclimation. Lau and coworkers (1996) showed that acclimation of the green alga, *Chlorella Vulgaris*, to a representative wastewater improved nutrient uptake and shortened retention times by an average of three days. It was also shown that the acclimation process did not alter the intrinsic growth properties of *C. vulgaris*. Matsumoto and coworkers (1995) found that a microalgae native to the region is easier to acclimate than one from far away. If acclimation is applied to the carbon dioxide fixation system, retention times could be decreased, resulting in smaller treatment cells with increased uptake efficiency.

Algal Harvesting Techniques

The four primary harvesting methods examined by Weissman and Goebel (1987) were microstraining, belt filtering, flotation with float collection, and sedimentation in two stages. It is important that harvesting not only remove the desired organism, but also any potential contaminants such as other types of cells and organisms. Any organism that the harvesting process fails to remove from the stream will be given a potentially significant competitive advantage in the growth pond. Therefore, it is essential that the harvester be universal in its removal capability.

Capital costs of the collection devices show that conventional dissolved-gas flotation units are most expensive, followed by belt filters, microstrainers, and settling ponds. However, it has been noted that none of the collection devices would function well on their own. Therefore, pretreatment options were considered. There is ample experience with chemical flocculation of suspended solids to improve separation characteristics. However, a rough calculation shows that if conditioner is added to the suspension prior to primary harvesting, production costs increase by about 10% for each \$0.01 of conditioner added per kilogram of biomass harvested. At present, the use of standard chemicals would require a dosage resulting in additional cost of about 4–6 cents per kilogram of biomass harvested. Thus alternatives to conventional flocculation are required.

One alternative to chemical conditioning is biomass conditioning via nitrogen deprivation. Nitrogen deprivation is recognized as a method to enhance the settling characteristics of algae if the biomass is starved for prolonged periods of time, well past any active growth. Some authors have reported that normally nonsettling, unicellular, flagellated organisms can be made to settle at high rates by short-term nitrogen deprivation. The universality of the process still poses a problem.

Another alternative is to utilize supersaturated oxygen or air to float the cells to the surface of the pond to a foam collector. The advantage over sedimentation lies in the fast rate of rise due to the dissolved gas coming out of solution. However, the universality of this approach is, again, open to question.

Experimentation with high-charge-density, high-molecular-weight polymers to flocculate a test organism has been performed. Results demonstrated that even small cells could be clarified by simple sedimentation when first pretreated with the polymer. The universality of this approach has also not been demonstrated, but the organism used provided a stringent test.

For all future work, it is recommended that the primary method of harvesting the biomass produced in a large, demonstration-scale system is pretreatment with polymer followed by sedimentation in a deep pond. The nitrogen-depleted condition of the biomass should promote flocculation and sedimentation. The slurry from the pond can be further concentrated in thickening tanks.

Beneficial Uses of Harvested Algae

Microalgae, once harvested from a cultivation pond or PBR, can be transformed into a useful product to offset capital and operational and maintenance costs. One promising option is as a combustible fuel in power plants and/or vehicles. Although the use of microalgae in power plants would not reduce overall carbon dioxide emissions, it could potentially reduce the carbon dioxide emissions per million Btu delivered by approximately 50% (Brown and Zeiler, 1993). Algae have similar combustion properties to coal, which makes cofiring an attractive option (Matsumoto et al., 1995). The integration of microalgal combustion with a coal-fired power plant could make the fuel less polluting with respect to carbon dioxide than existing oil- and natural gas-fired plants (Brown and Zeiler, 1993). Conversion of the harvested microalgae into a biofuel, such as biodiesel, could also be a viable alternative. Biodiesel is cleaner than petroleum diesel and is virtually free of sulfur, thereby eliminating the production of sulfur oxides. Emissions of hydrocarbons, carbon monoxide, and particulates during combustion are also significantly reduced. Another advantage is that biofuel may potentially be utilized in a standard, unmodified diesel engine (Brown and Zeiler, 1993). One species of algae, *Botryococcus braunii*, produces hydrocarbons up to 30% of its total weight (Usui and Ikenouchi, 1997). These hydrocarbons are easily extracted with ethyl acetate. The extracted oil has a similar calorific value to Class C fuel oil.

If commodity chemicals are produced from microalgae, carbon dioxide reductions can be significantly greater than if used for fuels. Products derived from microalgae include extraction products such as fatty acids, glycerol, protein, pigments, and sugars; bioconversion products such as alcohols, organic acids, and methane; and catalytic conversion products such as paraffins, olefins, and aromatics (Chelf et al., 1993; Michiki, 1995). Other products might include colorants, perfumes, vitamins, hydrogen production, and fodder for livestock (Michiki, 1995; Yanagi et al., 1995; Miura et al., 1995). In one experiment, algae added to a wood pulp, along with a polyacrylamide, improved density of the paper by filling void spaces (Hon-Nami et al., 1997). The gas permeability, smoothness, and ink absorptivity of the paper improved as well. The tensile strength decreased slightly, but was still within the satisfactory range of the standards. Another possible use of microalgae is as an additive to concrete (Usui and Ikenouchi, 1997). Polysaccharides, produced through photosynthesis, have been found to improve fluidity in concrete mixtures, reducing the need for compaction.

Bench-Scale Experiments

A bench-scale microalgal reactor system was established to verify growth without inhibition to flue gas constituents, verify algal growth rates reported in the literature, and develop a culture to assess potential beneficial uses of the harvested algae to provide data for the economic assessment. A schematic diagram of the bench-scale system is shown in Figure 3.

The algal reactor was a 12-inch-wide, 16-inch-high, 30-inch-long, 20-gallon glass aquarium. An operating volume of 16 gallons was established for testing. The sides of the aquarium were covered on the outside with a foam material to prevent light penetration through the sides of the reactor and provide incident light to the surface only. Light was provided by a two tube fluorescent fixtures with “Grow Light” tubes that are specifically designed to enhance plant growth. The reactor lights were controlled by a timer to simulate dark/light cycles of seasonal day lengths. The operating temperature was maintained at 104°F with a submersible heater. Dechlorinated tap water was added to the aquarium daily to offset evaporative losses.

Several attempts were made to optimize flue gas mass transfer, including flow absorber columns and spray scrubbers. However, at the small reactor scale and relatively low associated liquid flows, these systems were found to be impractical. As a result, a simulated flue gas was sparged through a fine-bubble diffuser at the bottom of the reactor. The sparge system was controlled using a solenoid valve to shut off the simulated flue gas flow during nonlight periods. The simulated flue gas was a blend of house compressed air and pressurized cylinders of CO₂, 10,000 ppm SO₂ in N₂,

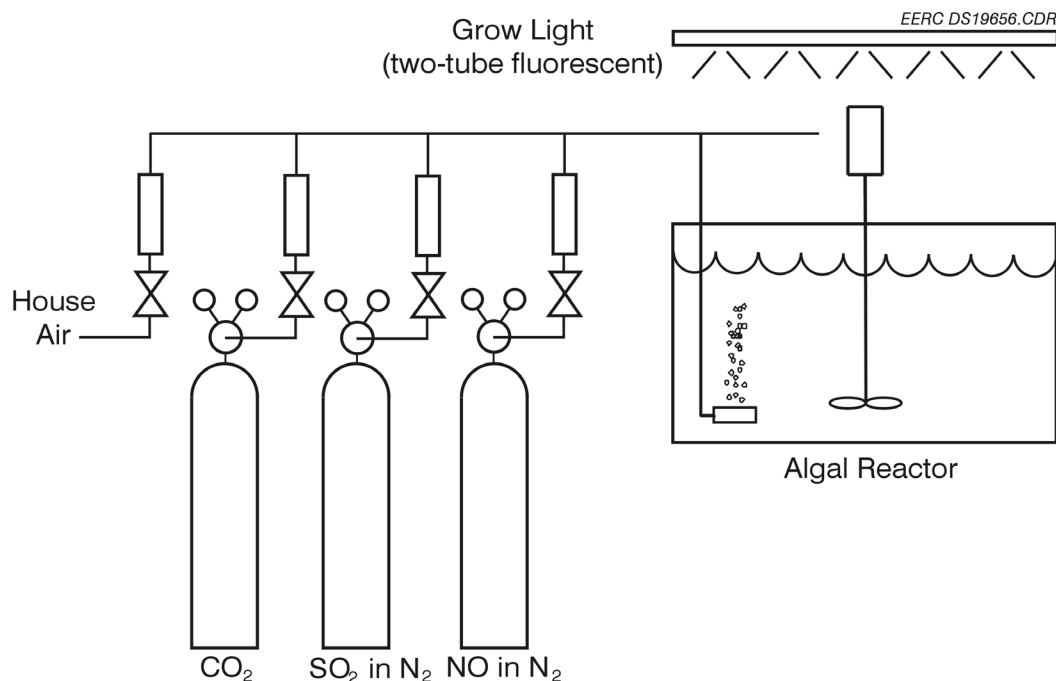


Figure 3. Bench-scale process diagram.

and 5000 ppm NO in N₂. The various gases were metered with rotameters into a common manifold to achieve mixing. The simulated flue gas was selected to be representative of the Coal Creek Station flue gas composition, as listed in Table 5.

The algae were cultivated in Bold's basal growth medium. Major constituents of the Bold's basal medium are listed in Table 6.

Table 5. Simulated Flue Gas Composition

CO ₂	12%
O ₂	5.5%
SO ₂	400 ppm
NO _x	120 ppm
N ₂	82%

Table 6. Bold's Basal Medium – Major Nutrients

H ₂ O, mL	Chemical	Grams	940-mL Medium Add, mL
400	NaNO ₃	10	10
400	CaCl ₂ · 2H ₂ O	1	10
400	MgSO ₄ · 7H ₂ O	3	10
400	K ₂ HPO ₄	3	10
400	KH ₂ PO ₄	7	10
400	NaCl	1	10

Several cultures of algae were acquired and used for testing. Preliminary testing utilized mixed cultures of green algae containing spirogyra, pandorina, scenedesmus micrasterias, and chlorella in Bold's basal medium that was cultured with a sparged flow of only CO₂ and air. Algal growth was monitored using settleable solids measurements – the volume of solids that settle from the algal growth medium in a 45-minute period using a 1-liter Imhoff cone. The solids content increased from 30 mL/L to 90 mL/L in the 2-month period of operation using CO₂ and air. After that period, SO₂ was added along with the CO₂ and air at a gas content of 12% CO₂, 5.5% O₂, 423 ppm SO₂, with the remainder as nitrogen in the gas flow. With continued operation over a period of about a month, a gradual change in the color of the algae from bright green to an olive drab color was also observed.

Microscopic examination of the algae revealed that no living algae cells were present. The flow of simulated flue gas was stopped, and compressed air was introduced to observe any recovery in algal growth.

Efforts were then made to obtain selected cultures of microalgae that had been reported to be resistant to higher levels of SO_x and NO_x , as reported in the literature. These include *Monoraphidium* and *Nannochloropsis* (National Renewable Energy Laboratory [NREL] strains Monor02 and Nanno02). A Biological Material Transfer Agreement was negotiated with the University of Hawaii Culture Collection, which maintained the NREL cultures. *Chlorella* sp. HA-1, *Galdieria* sp. (red alga), and *Chlorella* sp. T-1 cultures of *chlorella* were acquired from the University of Texas.

These cultures were initially direct-sparged with a simulated flue gas, less the contribution of SO_2 , which was added incrementally following a period of acclimation. These new cultures exhibited no apparent signs of inhibition to the SO_2 , but had different characteristics with regard to settleability. The new cultures did not agglomerate and settle readily from solution. As such, settleability measurements could not be used as an indicator of growth. Rather, growth was monitored by measuring absorbance with a spectrophotometer at a wavelength of 682 nm (APHA, 1975).

The cultures were grown in the presence of direct-sparged simulated flue gas for a period of approximately 3 months to develop a sample for the determination of relative protein, lipid, and carbohydrate fractions. Harvested samples were placed in frozen storage prior to the determinations.

The determination of lipids, proteins, and carbohydrates was carried out with a procedure very similar to that of Folch and coworkers (1957). The frozen algae sample was thawed, and a portion (8.0 g) of the wet paste was suspended in 50 mL of methanol and ultrasonicated for 1 minute in an Erlenmeyer flask. Chloroform (100 mL) was added, and the mixture was further ultrasonicated for 5 minutes. The mixture was filtered by gravity and the green residue scraped into a flask and again ultrasonicated with 150 mL of the 2:1 chloroform:methanol mixture. The mixture was filtered by gravity. The filtrates were combined and the solvents removed in a rotary evaporator. To remove moisture from the evaporated sample, 20 mL of dry ethanol was added and evaporated to azeotrope off the water. The green residue containing lipids and chlorophyll was weighed. The lipids exhibit the typical algae odor.

The residue from filtration was dried at 110°C and weighed to determine the amount of proteins plus carbohydrates. The dried residue was soaked overnight in 0.2 N perchloric acid (40 mL) to dissolve carbohydrates. The insoluble proteins were filtered by gravity and washed with 40 mL of DI water. The residue was dried at 110°C and weighed to determine the protein yield. The proteins are odorless.

The lipid content (26%) appeared to be fairly normal for algae, and it did not appear that large amounts of nitrogen were being fixed and promoting growth. Nor were the algae starving for nitrogen. The proteins made up 41% of the total mass, and carbohydrates were 33% (by difference).

PRELIMINARY ECONOMIC ASSESSMENT

Preliminary process economics were assessed based on the costs of CO₂ mass transfer, algal growth pond requirements, and algal harvesting compared to potential revenue from the assumed value from utilization of harvested algae (Figure 4). The assessment is based on a flue gas from a 550-MW coal-fired power plant. We assumed a 25% capture of CO₂ or the equivalent of 932 tpd of carbon, with operation for 12 hr/day, 365 days/year.

CO₂ Mass Transfer

Mass transfer economics were based on a 3:1 volume:volume ratio of flue gas to liquid, resulting in a 2,150,000-gpm water flow requirement. Mass transfer was assumed to be accomplished using M.W. Kellogg Weir scrubbers with a capacity of 450,000 cfm and a flow rate of 220 gal/1000 cfm (99,000 gpm) each. Although two weir scrubbers would be adequate based solely on the gas flow, the high liquid flow rate (2493 vs. 220 gal/1000 cfm) necessitates more scrubbers. A total of 22 weir scrubbers would be required to remove 25% of the CO₂. Based on a low-range scrubber installed cost (1995 basis) of \$350/kW, scrubbers for a 550-MW plant would cost approximately \$193 million.

Algal Growth/Photosynthesis

Assuming a CO₂ uptake rate of 2 g/L-day, a total CO₂ capture of 3418 tpd (932 tpd carbon), and a pond depth of 0.9 m (3 ft), the total surface area required for photosynthesis would be approximately 418 acres. Assuming a construction cost of \$40,000/acre for ponds of compacted clay liners with four mixers/acre and associated plumbing, the estimated pond capital cost is approximately \$17,000,000.

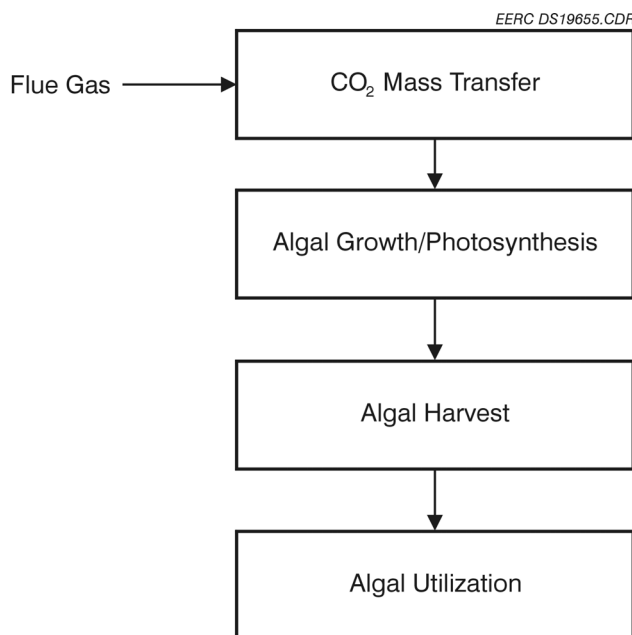


Figure 4. Carbon-sequestering unit operations.

Major nutrients, if not supplied in the flue gas, will be needed in order to support healthy algal growth. Nutrient requirements may be as high as 116 tons/day of ammonia at \$150/ton, 197 tons/day of diammonium phosphate at \$131/ton, and 42 tons/day of potash at \$78/ton as well as micronutrients. For purposes of this evaluation, a total annual operating cost for nutrients is estimated to be \$25,000,000.

Algal Harvest

Algal yields from this system are estimated to be 2136 dry ton/day (2427 ton/day, or 886,000 ton/yr at 12% moisture). The algae biomass will need to be harvested daily. Based on laboratory observations, typical water–solid clarifiers would be too large and too expensive to be incorporated as an algal separation technique. Since the water will be continually recirculated between the ponds and the scrubbers, a solids separation device such as a belt filter or a hydroclone should be incorporated to provide reliable harvesting. This operation was estimated to cost approximately \$20,000,000 for purposes of this evaluation.

Other costs associated with harvesting include drying of the moist algae. A capital cost of \$20,000 to dry the algae to a moisture content of 12% using waste heat from the power plant has been included. Electrical costs were estimated to be \$7,000,000 per year based on a 100-MW demand at \$0.015/kWh for year-round operation.

Economic Analysis Summary

A summary of economic factors is provided in Table 7. A total of \$250,000 was estimated for capital costs associated with mass transfer, photosynthesis ponds, and algal harvest operations. These costs were amortized over a 10-year period at an assumed loan interest rate of 9%. The annual cost of the loan is \$38,955,022. In addition, the total annual operating and maintenance costs, including nutrient costs, electricity, and labor, was estimated to be \$46,500,000. The resultant total costs of carbon sequestering under this scenario for a 550-MW power plant would be approximately \$85,455,022.

A revenue stream in the form of harvested algae can offset the total costs. In this evaluation, an estimated 886,000 tons of algae at 12% moisture content would be harvested. In order to offset the cost of using this type of system for carbon sequestration, a value of approximately \$96.45 would be need to be recovered from the harvested algae.

Raw algae is of little value because of its general impalatability to animals, limiting its use as an animal feed. However, separation of the relative fractions of protein, lipid, and carbohydrate in the harvest algae can result in marketable products. Based on the presented analysis, the potential for beneficial uses of the harvested algae are illustrated in Figure 5. The relative fractions of protein,

Table 7. Preliminary Process Economics Evaluation

COSTS		
<u>Capital Cost</u>		
Scrubbers	\$193,000,000	
Ponds	\$17,000,000	
Algae Separation	\$20,000,000	
Algae Drying	\$20,000,000	
Total Capital Cost	\$250,000,000	
<u>Capital Amortization</u>		
Principal	\$250,000,000	
Interest Rate	9%	
Life of Loan (years)	10	
Annual Payment	\$38,955,022	\$38,955,022
Total Cost of Loan	\$389,550,225	
<u>O&M Cost</u>		
Electricity	\$16,500,000	
Fertilizer	\$25,000,000	
Salaries	\$5,000,000	
Total O&M Cost	\$46,500,000	\$46,500,000
Total Annual Cost (Capital + O&M)		\$85,455,022
REVENUE		
Algae Production Rate (ton/yr@ 12% moisture)	886,000	
Algae Unit Value	\$96.45	
Total Annual Algae Revenue	\$85,455,023	\$85,455,023
NET ANNUAL PROFIT		\$0
BENEFIT/COST RATIO		1.00
PAYBACK PERIOD (years)		4.56

lipid, and carbohydrates, were 41%, 26%, and 33%, respectively. At an algal harvest rate of 2427 tpd at 12% moisture (2136 tpd dry weight), approximately 876 tpd of protein could be recovered and used as an animal feed. Similarly, an estimated 555 tpd of lipids could be recovered for use in the production of liquid fuels and chemicals. Approximately 705 tpd of carbohydrates would also be recovered. These carbohydrates may be suitable as a fermentation feedstock for the production of alcohols or organic acids.

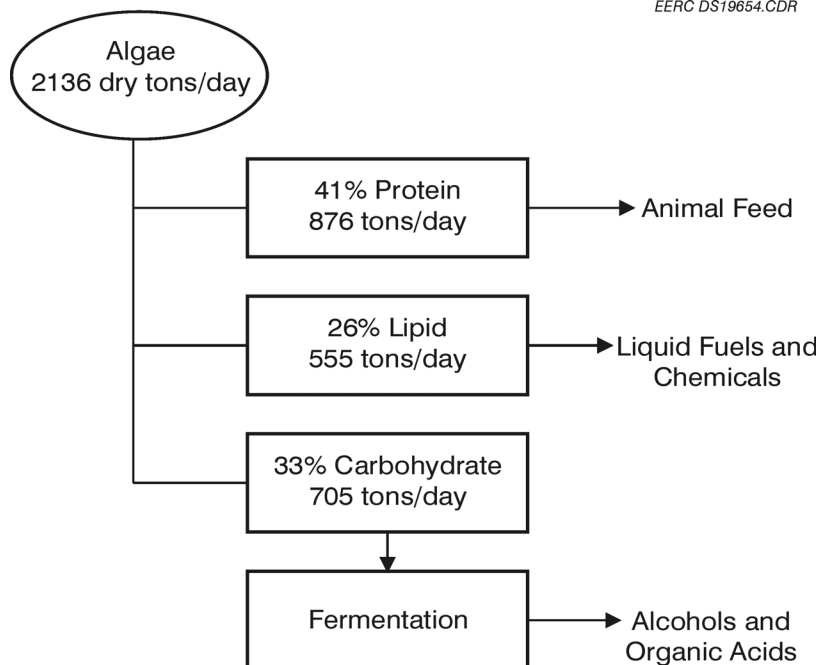


Figure 5. Beneficial uses of harvested algae.

CONCLUSIONS

The results of this project have verified the potential applicability of using microalgae biofixation to sequester carbon dioxide from flue gas at coal-fired power plants. The results indicate that an algae-based system is feasible without the need for technological breakthroughs, but key design criteria need to be further developed, including CO₂ mass transfer, algal growth rates, and developing strategies to produce a revenue stream from the harvested algae.

Specific strains of certain algae (*Monoraphidium* strain MONOR02 and *Nannochloropsis* NANNO02) were successfully grown under directly sparged simulated flue gas consisting of 87% N₂, 12.1% CO₂, 5.5% O₂, 423 ppm SO₂, and 124 ppm NO_x.

Harvested algae were shown to consist of 41% protein content, 26% lipid content, and 33% carbohydrate (by difference). A preliminary economic assessment indicated that nearly \$97 per ton of harvested algae would be required in order to recover capital and operating and maintenance costs. The analysis indicated the potential to produce 2427 tpd of algae at 12% moisture (2136 tpd dry weight). Of this, approximately 876 tpd of protein could be recovered and used as an animal feed. Similarly, an estimated 555 tpd of lipids could be recovered for use in the production of liquid fuels and chemicals. Approximately 705 tpd of carbohydrates would also be recovered. These carbohydrates may be suitable as a fermentation feedstock for the production of alcohols or organic acids.

Continued work should focus on the development of cost-effective methods of CO₂ mass transfer techniques, the most expensive unit operation using the evaluated scenario. Algal growth

rates and CO₂ uptake rates under field conditions should be further developed at a larger scale to provide more reliable data for the process development and economic models. Further, new studies need to be conducted to develop cost-effective methodologies to separate the lipid, protein, and carbohydrate fractions so that the production of high-value products can be realized.

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